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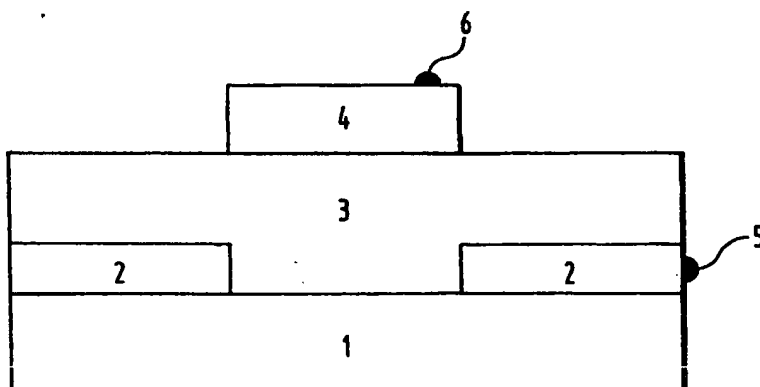
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(54) Title: POLYMER-NANOCRYSTAL PHOTO DEVICE AND METHOD FOR MAKING THE SAME



(57) Abstract

The present invention relates to a photo device comprising a layer of nanometer sized particles and a conducting polymer in solid state, wherein the nanometer sized particles are chosen from the group of  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{CdSe}$ ,  $\text{CdS}$ ,  $\text{ZrO}_2$  and  $\text{SnO}_2$ ; and wherein the conducting polymer comprises PPV (polyparaphenylenevinylene) or a derivative thereof.

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POLYMER-NANOCRYSTAL PHOTO DEVICE AND  
METHOD FOR MAKING THE SAME

Especially for reducing costs for photovoltaic cells, research is done all around the world for finding a solid state composition of creating an interpenetrating solid-state conducting material in a nanoporous network.

5 Such device could also be used for LED (Light Emitting Diodes), photo sensors, optical switches and even optical networks.

The present invention relates to a photo device comprising a layer of nanometer sized particles and a  
10 conducting polymer in solid state, wherein the nanometer sized particles are chosen from the group of  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{CdSe}$ ,  $\text{CdS}$ ,  $\text{ZrO}_2$  and  $\text{SnO}_2$ , and wherein the conducting polymer comprises PPV (polyparaphenylenevinylene) or a derivative thereof.

15 Prior methods have been published on the insertion of a polymer electrolyte into a preformed nanocrystalline  $\text{TiO}_2$  (titanium dioxide) network (F. Cao et al., Proceedings of Nanostructured Materials in Electrochemistry, held: Reno, NV, USA, 21-26 May 1995).  
20 These methods have, however, the disadvantage of being based on an ionic conductor. The device performance is therefore limited. The ionic conductor is not suited for electronic devices.

Another prior method using conducting  
25 polymers (PPV and derivatives) replaces the inorganic nanocrystalline network with  $\text{C}_{60}$  and derivatives which act as electron-acceptors (G. Yu et al., Science 270 (1995) 1789). However, in this method, the electron transport is restricted. Further,  $\text{C}_{60}$  is not a material which is  
30 produced abundantly, and is expensive; it is also much less stable than inorganic materials.

Another prior method using a conjugated polymer, poly(2-methoxy, 5-(2'-ethyl)-hexyloxy-p-phenylenevinylene; MEH-PPV), incorporates nanoparticles of CdS or CdSe (N.C. Greenham et al., Physical Review B. Condensed Matter, 54 (1996) 17628, N.C. Greenham et al., Synthetic Metals 84 (1997) 545-546), but the cadmium-containing compounds have a disadvantage in that they are carcinogenic and also not abundantly available.

Another publication (S.A. Carter et al., Applied Physics Letters 71 (1997) 1145) discloses the use of TiO<sub>2</sub> nano-particles blended with electroluminescent organic material in light emitting diodes. As an example, MEH-PPV was tested as organic material. The mixtures were spin cast onto an Ito coated glass, whereafter the solvent was evaporated off. The device lacks photovoltaic properties.

The present invention has for its object to offer a solution to the problem of creating an interpenetrating solid-state conducting material in a nanoporous network, for the purpose of creating stable, all-solid state photovoltaic cells. The instability problems associated with liquid based electrolytes in nanoporous networks (B. O'Regan et al., Nature, 353 (1991) p737) are to be avoided.

A further object of the present invention is to offer a photovoltaic cell, which offers the stability, electron transporting properties, the abundant availability, the low costs, and the no-toxicity of TiO<sub>2</sub> in an interconnected network in combination with the hole-transporting, light-absorbing, stable properties of PPV (poly-paraphenylenevinylene).

A further aspect of the present invention is the ease of manufacturing, namely in a single thermal treatment of the inorganic and organic materials together. The thermal treatment is elegantly simple, and provides for converting the polymer precursor to its final, conducting form as well, as for producing electrical contact between the inorganic nanometer sized

particles to make continuous electron-carrying pathways to the end terminal of the photovoltaic cell, the object of the present invention.

None of the above prior art methods use a mixture of a polymer precursor in solution and inorganic nanometer sized particles in a colloidal solution to produce an interpenetrating composite layer in a single step of thermal treatment.

A preferred embodiment of the method according to the present invention uses a conducting polymer precursor (poly(p-xylylene-alpha-tetrahydrothiophene-bromide; p-PPV) and a nanocrystalline material,  $\text{TiO}_2$ .

Further advantages, features and details of the present invention are elucidated in the following description, which refers to the enclosed figures, in which:

fig. 1 is a diagrammatic cross section view of a device according to the present invention; and

fig. 2 is a graph of current voltage characteristic of the device of fig. 1.

A schematic cross section of the cell is shown in fig. 1. The polymer p-PPV was made by chemical synthesis (J.J.M. Halls et al., Nature 376 (1995) 498), the  $\text{TiO}_2$  nanocrystals were obtained from Degussa AG Corporation, Germany. An approximately 0.7% methanolic solution of the p-PPV was combined with a colloid of  $\text{TiO}_2$  (the colloid had been made according to Nazeeruddin et al., J. Am. Chem. Soc. 115 (1993) 6382), to give a mixture of approximately 1:1 p-PPV and  $\text{TiO}_2$  by weight. This mixture was spin-coated on a glass substrate 1 with a transparent conducting coating 2, in this example  $\text{SnO}_2:\text{F}$ , to give a thin film 3. The film was heated to  $320^\circ\text{C}$  for ten hours in vacuum and an aluminum contact 4 was evaporated in such a way that there was no overlap with the transparent conducting coating on the glass on top of the film to complete the cell.

Current-voltage (IV) curves of the cells in the dark and in substantially white light were measured at

terminal 5 and 6 (fig. 1) and a plot of this data is shown in fig. 2 which demonstrates that the cells produce electric power under illumination.

At least the thermal treatment step of the present invention is novel and inventive over the prior art. This step provides for both conversion of the p-PPV to its conducting form, PPV and for producing electrical contact between the  $\text{TiO}_2$  particles to produce electron-carrying paths through the film.

The method according to the present invention allows the use of precursor polymer and thus the complex process of first synthesizing MEH-PPV before blending with nanoparticles. Moreover, the method, by starting from a mixture of a colloid of  $\text{TiO}_2$  and a solution of p-PPV, also provides a solution to the very poor penetration of conducting polymers with high molecular mass into a preformed porous nanocrystalline semiconductor.

The present method is first in making operational photovoltaic cells of a conducting polymer, such as PPV, and a sintered electrically interconnected network of nanocrystalline particles, such as  $\text{TiO}_2$ .

PPV has been shown to be a good hole-conducting material and  $\text{TiO}_2$  an excellent electron transporter, so their combination together, prepared in a single thermal treatment step, provides a significant advantage.

The present invention is not limited to the embodiment described; the rights applied for are defined in the annexed set of claims; the scope of protection includes other polymers and nanocrystals, as well as other temperatures.

## CLAIMS

5

1. A photo device, comprising a layer of nanometer sized particles and a conducting polymer in solid state.

2. A photo device according to claim 1, wherein  
10 the nanometer sized particles are chosen from the group of  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{CdSe}$ ,  $\text{CdS}$ ,  $\text{ZrO}_2$ ,  $\text{SnO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ .

3. A photo device according to claim 1 or 2, wherein the conducting polymer is a conjugated polymer with the functionalities of light absorption and charge  
15 transporting properties.

4. A photo device according to claim 1, 2 or 3, in which the conjugated polymer comprises PPV (polyparaphenylenevinylene) or a derivative thereof.

5. A photo device according to claim 1, 2, 3 or  
20 4, wherein the layer is a thin film of a photovoltaic cell.

6. A method for producing a photo device, according to claim 1, wherein the layer is made by mixing the nanometer sized particles in a colloid with precursor  
25 PPV.

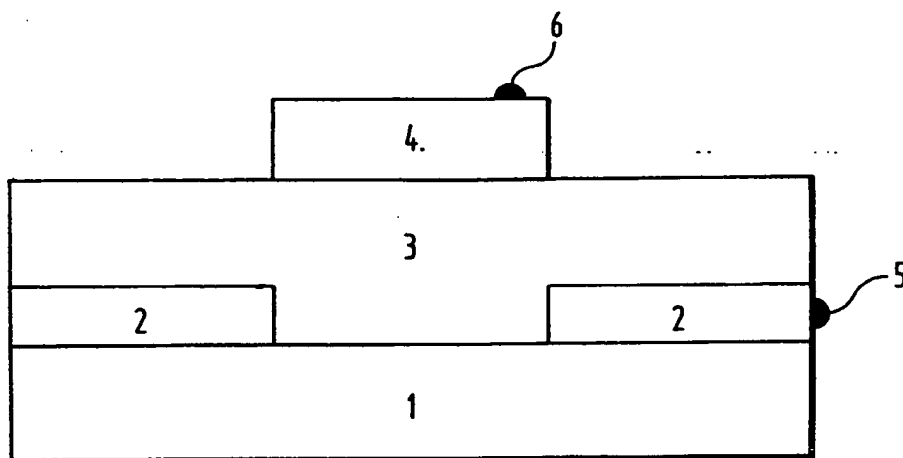
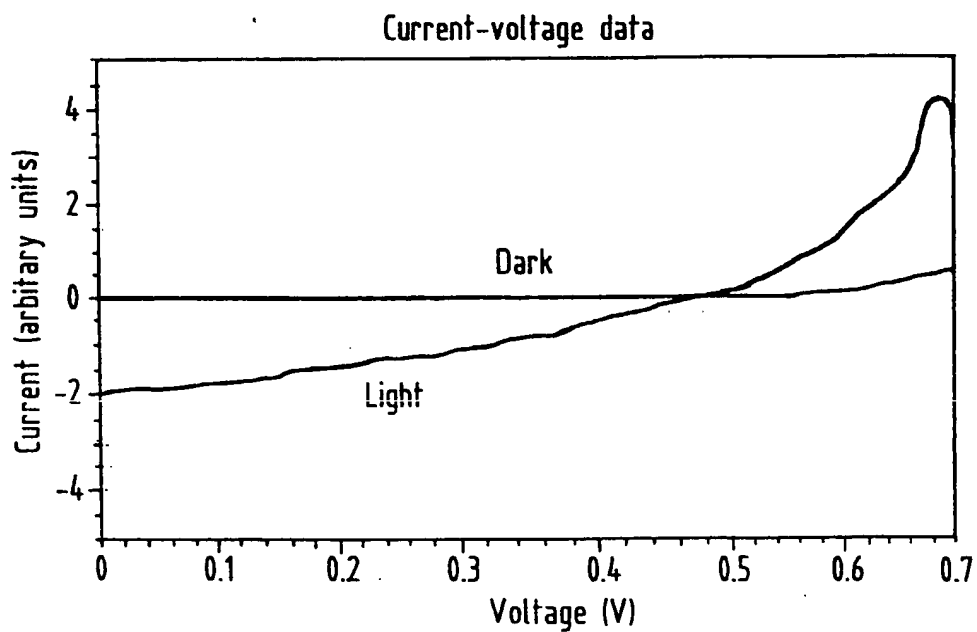
7. A method according to claim 6, wherein the precursor PPV is poly(p-xylene-alpha-tetrahydrothiophene bromide).

8. A method according to claim 6, wherein the  
30 mixture of  $\text{TiO}_2$  and PPV is between 10:90 and 70:30 by weight.

9. A method according to claim 6, for producing a photo device, according to claim 1, wherein the layer is heated to a predetermined temperature during a  
35 predetermined time.

10. A method according to claim 9, wherein the heating takes place in an inert gas, at substantially underpressure, or vacuum.

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FIG. 1FIG. 2



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 98/07328

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 H01L31/0384 H01L51/20 H01L51/30 H01L33/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	N.C. GREENHAM ET AL.: "Charge separation and transport in conjugated-polymer/semiconductor-nanocrystal composites studied by photoluminescence quenching and photoconductivity" PHYSICAL REVIEW, B. CONDENSED MATTER., vol. 54, no. 24, 15 December 1996, pages 17628-17637, XP002060964 NEW YORK US cited in the application see page 17628 - page 17630 — —/—	1-5

☒ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

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Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	N.C. GREENHAM ET AL.: "Charge separation and transport in conjugated polymer/cadmium selenide nanocrystal composites studied by photoluminescence quenching and photoconductivity" SYNTHETIC METALS, vol. 84, no. 1-3, 1 January 1997, pages 545-546, XP002060965 AMSTERDAM, NL cited in the application see the whole document	1-4
X	S.A. CARTER ET AL.: "Enhanced luminance in polymer composite light emitting devices" APPLIED PHYSICS LETTERS., vol. 71, no. 9, 1 September 1997, pages 1145-1147, XP000720223 NEW YORK US cited in the application see page 1145	1-4
A	KUCZKOWSKI A: "THE PROSPECTS FOR POLYESTER POLYMER-CDS POWER COMPOSITES IN PHOTOELECTRONIC DEVICE APPLICATIONS" JOURNAL OF PHYSICS D. APPLIED PHYSICS, vol. 22, no. 11, 14 November 1989, pages 1731-1735, XP000072966 BRISTOL, GB see the whole document	1-5,9,10
A	HALLS J J M ET AL: "EFFICIENT PHOTODIODES FROM INTERPENETRATING POLYMER NETWORKS" NATURE, vol. 376, 10 August 1995, pages 498-500, XP000578123 cited in the application see the whole document	1,3-5,9,10